



Technical Note N-1250

INVESTIGATION OF CHEMICAL CROSSLINKING OR COMPLEXING OF
WATER-SOLUBLE MATERIALS TO YIELD WATER-INSOLUBLE MATERIALS

By

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ABSTRACT

In an effort to produce resinous compounds for use in preventing passage of water through porous construction materials such as concrete, a series of crosslinking or complexing reactions were carried out to produce water-insoluble materials from water-soluble materials. None of the materials produced had mechanical and chemical properties equal or superior to those of polyvinyl alcohol precipitated by sodium sulfate.

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INTRODUCTION

In the present consideration of materials for construction of deep ocean fixed structures, the emphasis is on the use of materials such as metals and concrete. However, when one considers that the proposed structures will probably be required to remain at great depths for long periods, then such problems as corrosion of metals and water permeability of concrete must be considered. The objective of this study was to investigate the possibility of formation of resins in porous materials such as concrete to prevent the passage of water through these materials.

Work has and is being done to form resins (plastics) in porous materials to improve their dimensional stability and moisture resistance. The processes which give desirable results consist of either (1) impregnation of the porous material with methyl methacrylate followed by radiation polymerization, or (2) impregnation of the material with methyl methacrylate, catalyst, and promoter followed by heating to polymerize the monomer.

However, each of these processes has disadvantages. Radiation cure involves all of the problems inherent in maintaining and operating a high energy radiation source, and catalyst plus heat cure involves the use of organic peroxides with the hazard of a sudden explosion.

Therefore, two other methods, chemical crosslinking by reaction between two or more compounds and complex formation between two or more compounds were investigated to determine their suitability for the formation of insoluble resins in-situ.

Three constraints were placed on the selection of starting materials for these reactions:

1. The materials be soluble in aqueous solutions rather than requiring organic solvents which create problems in recovery and in pollution.
2. The materials used should have low toxicity so that they could be easily handled during treatment of a structure or structural components and so that any waste or residual materials would not have a deleterious effect on the environment.
3. The materials should be commercially available at low to moderate cost.

The initial phase of the work was a literature survey on the crosslinking of water-soluble polymers.



LITERATURE SURVEY ON CROSSLINKING REACTIONS

Polyvinyl Alcohol

Polyvinyl alcohol is widely used in the manufacture of water-soluble films for packaging. Fibers can be produced by passing an aqueous solution of polyvinyl alcohol through spinnerets into an aqueous solution of sodium sulfate, after which it is crosslinked with formaldehyde.¹ Direct formaldehyde crosslinking of polyvinyl alcohol has also been accomplished in the presence of mineral acids,^{2,3} and acrolein (at pH 6.5)⁴ and polyacrolein (in neutral and acid solution)⁵ have also been used. Aldehydes⁶ and aldehyde reaction products,^{7,8} aliphatic dicarboxylic acids usually in the presence of mineral acids,⁹⁻¹² quinone,¹³ formamide,¹⁴ N,N-methylenesbisacrylamide,¹⁵ N-methylolacrylamide,¹⁶ 5-hydroxy-5-H-dibenz [c,e] azepine,¹⁷ esters of propionic acid,¹⁸ dimethylene thiourea,¹⁹ trichloroethyl phosphite and diacetoxysiloxane,²⁰ and cyanuric chloride,²¹⁻²³ maleic anhydride,²⁴ methacrylic acid,²⁴ polyamide-epichlorohydrin resin,²⁴ and poly (vinyl-methyl ether/maleic anhydride)²⁵ have been reported as crosslinking agents for polyvinyl alcohol.

Insolubilization, gelation, or crosslinking of polyvinyl alcohol can occur when it is treated with inorganic compounds such as ammonium perborate,²⁶ cupric ion,²⁷ hydrochloric or sulfuric acid,²⁸ cupric dichromate,²⁴ and ammonium zirconyl carbonate.²⁹

Acrylamide and Polyacrylamide

Mixtures of acrylamide and N,N-methylenebisacrylamide can be polymerized and crosslinked in dilute aqueous solutions^{30,31} to form stiff gels for soil stabilization. Polyacrylamide, when crosslinked with polyacrolein, forms a tough, clear, insoluble gel, but when cross-linked with gelatin, cellulose polymethyl ether, or polyvinyl pyrrolidone, viscous solutions are formed.³⁴

Other Compounds

Methyl cellulose can be crosslinked by the dipropiolate of polyethylene glycol (MW 300) to yield films which are highly softened by but insoluble in cold or boiling water.¹⁸ Dimethylol urea, dialdehyde starch, glyoxal, and formaldehyde crosslink gelatin and the dipropiolate of tetraethylene glycol reacts with starch to form a compound which is insoluble in cold and boiling water.³⁵ Polyacrolein treated with ethylene glycol yields a highly crosslinked film which is insoluble in boiling water.⁵ Poly(methylvinyl ether/maleic anhydride) (PVM/MA) reacts with di-, tri-, and polyhydroxy compounds to form materials with some water resistance.²⁵ A crosslinked ester is formed when PVM/MA reacts with 2-butene-1,4-diol and polyvinylpyrrolidone in solution.³⁶ Copolymers derived from vinylpyrrolidone and water-insoluble comonomers

can be crosslinked by heating to 150°C, but greater water resistance can be obtained by the use of a dibasic acid, especially succinic acid.³⁷

Dimethylol urea will crosslink compounds with hydroxyl, carboxyl, amide and amino groups to form compounds with reduced water solubility. For example, the reaction product of dimethylol urea and urea has been used as a wood impregnant.³⁸ Reaction products with formaldehyde,³⁹ urea,⁴⁰ and phthalic anhydride⁴¹ have been used to treat fabrics. Other insoluble products have been made by the reaction of dimethylol urea with polyamino compounds,⁴³ formaldehyde in butanol,⁴⁴ butanol,⁴⁵ furfuryl alcohol,⁴⁶ furfuryl alcohol plus formaldehyde,⁴⁷ alcohol soluble butyric acid esters of cellulose,⁴⁸ allyl alcohol,⁴⁸ cellulose,⁵⁰ partially hydrolyzed starch,⁵⁷ potato flour,⁵² ground corn cobs and salicylic acid,⁵³ silicic acid,⁵⁴ and alkyl silicates.⁵⁵

EXPERIMENTAL

The following reactions were conducted after a review of the literature. They were chosen because they essentially met the three constraints mentioned in the Introduction.

Polyvinyl Alcohol

Experiment 1. Polyvinyl alcohol (4.5 g.) was slurried with cold water (30 ml.) and heated, with stirring, until a solution was obtained. A quantity of the solution was poured into 20 percent sodium sulfate solution. A tough elastomeric solid precipitated. It was soluble in boiling water, but had good resistance to cold water.

Experiment 2. Polyvinyl alcohol (45 g.) was slurried with 300 ml. of cold water, then heated to about 88° for 60 minutes. Additional water was added to lower the viscosity of the solution. After cooling, thiourea (7.6 g.) in water (100 ml.) and formalin solution (20 g., 36.6%) were added and the solution was heated to 85° for 1½ hours and allowed to cool. A sample was poured into 20 percent sodium sulfate solution and a tough elastomeric solid formed. It dissolved in boiling water, had good resistance to cold water, but was not superior to precipitated polyvinyl alcohol.

Experiment 3. Polyvinyl alcohol (11 g.) was slurried with and then dissolved in water (89 ml.) at 88°C. After cooling, ethylenediamine (0.2 g.) and a suspension of cyanuric chloride (3.3 g.) in acetic acid (10 ml.) were added. The mixture was stirred vigorously, and ten percent sodium hydroxide solution was added to maintain an alkaline condition during the addition of the cyanuric chloride. A white suspension formed, and a small quantity of this suspension was poured into a Petri dish and dried under an infrared heat lamp. The film which formed was not water resistant.

Experiment 4. Polyvinyl alcohol (12 g.) was slurried with 88 ml. of cold water, then heated with stirring to effect solution. Additional water was added to lower the viscosity. Oxalic acid (3 g.) and glycerol (10 g.) were added, stirring was continued, the temperature of the solution was raised to 95°, and heating was continued for one hour. Then the solution was set aside to cool. A sample was transferred to a Petri dish and heated to 100° under an infrared lamp to drive off water; then it was heated at 135° for three hours and cooled to room temperature. A sample of the tough film which had formed lost its strength in boiling water and in cold water.

Experiment 5. In a 500 ml. round-bottomed flask were placed 4,4'-sulfonyldiphenol (dihydroxydiphenylsulfone) (25 g.), formalin (36 g., 36.6%), sodium hydroxide (8 g.), and water (72 g.). A solution formed and was refluxed for 6½ hours and allowed to cool to room temperature. Sodium bisulfite (5 g.) was added and dissolved. The solution was poured into a 1000 ml. beaker, ice was added, and the solution was acidified with 20% sulfuric acid. A white precipitate formed and was collected on a Buechner filter, was washed with water, and was sucked as dry as possible. The damp solid was transferred to an evaporating dish, cut into small pieces, and set aside to dry. When dry it was powdered. Then 0.05 g. was added to a methanol-water solution of polyvinyl alcohol (0.45 g.) and dissolved. A portion of the solution was poured into a Petri dish, dried at room temperature, and heated at 150° for one hour. The film which was produced was resistant to cold water. When the film was formed by casting on a Teflon^R sheet, drying at room temperature and heating at 150° for one hour, it broke without yielding and lost strength when immersed in water.

Acrylamide

Experiment 1. Polyacrylamide (6 g.) was mixed with water (194 ml.) in a blender, after which 0.25 percent dialdehyde starch solution (5 g.) was added and the pH adjusted to two with concentrated hydrochloric acid. A sample was poured into a Petri dish and heated under an infrared lamp. The film which formed was not water resistant.

Experiment 2. A solution containing 35 g. of a mixture of acrylamide and N,N-methylenbisacrylamide in 80 ml. of water was mixed with 15 g. of an aqueous solution containing five percent polyvinylpyrrolidone and 2.5 percent sulfur dioxide (as sulfurous acid). An exothermic reaction occurred, and within a few minutes, a gel had formed. When placed in cold water the gel absorbed water and softened.

The experiment was repeated except that gelatin was used instead of polyvinylpyrrolidone. Again, an exothermic reaction yielded a gel. When placed in cold water, the gel absorbed water and softened. Similar results were obtained when neither polyvinylpyrrolidone nor gelatin were used.

Other Compounds

Experiment 1. Poly(vinylmethyl ether/maleic anhydride) (1 g.) was dissolved in 2-butanone (9 g.) and ethylene glycol (0.4 g.) was added and stirred in. A quantity of this solution was poured into a Petri dish, carefully evaporated to dryness, and heated under an infrared lamp at 140° for 15 minutes. The thin friable film which was produced resisted water at ambient temperature, but broke up in boiling water.

Similar results were obtained when ethylene glycol (0.4 g.) was mixed with 10 g. of a ten percent aqueous solution of poly(vinylmethyl ether/maleic anhydride).

Experiment 2. Poly(vinylmethyl ether/maleic anhydride) (20 g.) was dissolved in hot (90-96°) water. 2-Butyne-1,4-diol (11 g.), N-vinylpyrrolidone (7 g.) and benzoyl peroxide (0.9 g.) were added and the mixture was stirred vigorously. Heating a sample of this material on a Teflon^R sheet at 160° for ten minutes with an infrared lamp yielded a dark brown, water-soluble solid.

Experiment 3. To 20 g. of a ten percent aqueous solution of poly(vinylmethyl ether/maleic anhydride) were added 1.1 g. of 2-buten-1,4-diol, 0.7 g. N-vinylpyrrolidone and 0.1 g. of α,α' -azodiisobutyronitrile. After stirring, a portion of the resulting mixture was poured into a Petri dish, evaporated to dryness, and heated to 140° for approximately 30 minutes under a heat lamp. The dark brown, friable film which was produced was resistant to cold and boiling water.

Experiment 4. A two percent aqueous solution of sodium carboxymethyl cellulose (10 g.) and a ten percent aqueous solution of poly(vinylmethyl ether/maleic anhydride) were mixed. A disc of filter paper was dipped into the resulting solution, dried, and then heated at 150° for ten minutes under an infrared heat lamp. The paper was placed in boiling water for 15 minutes. The film remained in the paper, but was not impervious to water.

Experiment 5. Succinic acid (0.1 g.) was added to a copolymer of vinylpyrrolidone and ethyl acrylate (20 g.) and stirred. A sample was poured on a Teflon^R sheet, warmed with an infrared heat lamp to drive off moisture, then heated at 140° for 45 minutes. The film which formed was softened by but not dissolved by boiling water or by cold water.

Experiment 6. Dimethylol urea (120 g.) was mixed with formalin solution (110 g., 36.6%), butanol (30 ml.) and 28 percent sodium hydroxide solution (6 ml.) in a 1 l. round-bottomed flask and refluxed for 45 minutes. Urea (9 g.) was added and refluxing was continued for an additional 45 minutes, after which butanol (100 ml.) was added and the solution was refluxed for 20 minutes. Oxalic acid solution (6 ml., 6.15%)

and butanol (14 ml.) were added, refluxed for 15 minutes, butanol (30 ml.) was added and refluxing was continued until a clear solution was obtained (approximately 24 hours). Water and butanol were removed by distillation and fresh butanol was added to the pot to keep the volume constant. After 470 ml. had distilled, the contents of the pot were anhydrous. Films formed from this product by evaporation of the solvent and heating were not water resistant.

Experiment 7. Dimethylol urea (12 g.) and formalin (16.3 g.) were mixed in a 125 ml. Erlenmeyer flask. Sodium hydroxide solution (10%) was added to make the mixture alkaline. On heating, a solution formed, melamine (8.4 g.) was added, and heating was again continued until a solution formed. The solution was set aside to cool. A quantity of the cool solution was applied to filter paper and heated. The friable film bubble which formed was essentially unaffected by boiling water.

CONCLUSIONS

1. From the results of the literature survey and laboratory experimentation, it is concluded that none of the materials produced by crosslinking or complexing would be suitable for forming water-insoluble resins in-situ in a porous material. None had properties equal or superior to precipitated polyvinyl alcohol.

2. Precipitated polyvinyl alcohol shows promise as a waterproofing agent for porous construction materials.

FUTURE PLANS

No further search for water-insoluble resins, formed by chemical crosslinking or complexing of water-soluble compounds, is planned.

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